

## RAW MATERIALS

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### SYNERGISM OF ORGANO-MINERAL DEFLOCCULATORS IN CERAMIC SLIPS

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It is shown that complex organo-mineral deflocculators based on oxyphenol furfural oligomers affect the surface tension at a liquid-gas boundary as well as the contact angle and wetting energy of aluminum oxide, marble and quartz surfaces. The phenomenon of synergism accompanying the introduction of complex organo-mineral deflocculators with the optimal components ratios in ceramic slips containing aluminum-oxygen compounds is confirmed.

**Key words:** complex organo-mineral deflocculators, ceramic slips, aluminum-oxygen compounds, contact angle, surface tension, wetting energy, phenomenon of synergism.

Ceramic slips comprise a complex multicomponent system, in which the solid phase is represented by small particles of kaolin, clay and other minerals and the liquid phase by a solution of electrolytes. It is known that the  $Al^{3+}$  ions present in these dispersions enhance structure formation and decrease fluidity [1]. In this connection the use of individual electrolytes in ceramic slips is ineffective for achieving the required aggregate stability and mobility. For this reason other modifiers must be introduced additionally in order to regulate structure formation and the physical-chemical properties of polymineral suspensions.

Complex deflocculators make it possible to obtain competitive ceramic articles with improved physical-mechanical properties as well as to expand the assortment of ceramic wares and lower the energy consumption in their production and the production costs of the finished product. However, the assortment and production volumes of such deflocculators are small, there no such products in the domestic market and expensive foreign analogs are used in the ceramic enterprises in the Russian Federation. For this reason it is important to develop a technology for obtaining domestic high-efficiency complex deflocculators for ceramic slips and to study the mechanism of their action.

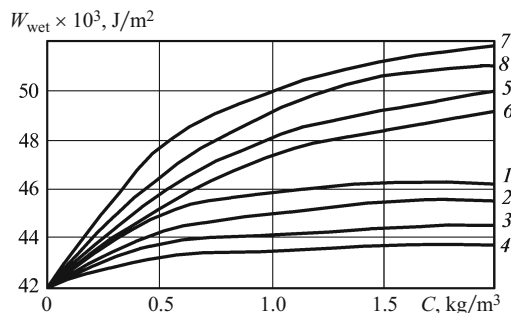
Previously, we synthesized experimentally highly effective two- and three-component organo-mineral complexes based on the fluoroglycine furfural oligomer SB-FF and the product of polycondensation of the vat residue from the production of resorcin with furfural SB-5 in a complex with sodium tripolyphosphate STPP and sodium hydroxide for mineral suspensions and ceramic slips based on them, containing aluminum oxygen compounds in a disperse phase. It was determined experimentally that for a definite ratio of the components in two-component complexes (SB-FF + STPP  $\approx$  1:4; SB-5 + STPP  $\approx$  1:4) and three-component complexes of deflocculators (SB-FF + STPP + NaOH  $\approx$  1:3.75:1.5; SB-5 + STPP + NaOH  $\approx$  1:3.75:1.5) synergism is observed — a mutual intensification of the action of components simultaneously introduced into polymineral suspensions containing aluminum compounds. The complex organo-mineral deflocculators which we developed are highly effective in such systems at content 0.1 – 0.15% of the solid-phase mass. As the fraction of the aluminum oxygen compounds in the ceramic slips increases, the action of the initial components of the additives becomes less effective, but the synergism of the complex deflocculators increases [2 – 6].

It is known that the methods used for thinning ceramic slips rely on the laws of colloidal chemistry, which describe the ion-exchange and adsorption phenomena occurring on the surfaces of particles of a disperse phase. The strength of coagulation contacts between the particles of a disperse phase and the free specific surface energy at a disperse phase

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**Fig. 1.** Effect of the content  $C$  of different additives on the wetting energy  $W_{\text{wet}}$  of the surface of aluminum oxide  $\text{Al}_2\text{O}_3$ : 1) SB-FF; 2) SB-5; 3) STPP; 4) NaOH; 5) SB-FF + STPP; 6) SB-5 + STPP; 7) SB-FF + STPP + NaOH; 8) SB-5 + STPP + NaOH.

— dispersion medium interface decreases by the amount of the wetting energy [7].

For this reason, to confirm the phenomenon of synergism of complex organo-mineral defloculators based on oxyphenolfurfural oligomers occurring with increasing fraction of the aluminum oxygen groups in ceramic slips we studied the effect of the components of complex organo-mineral defloculators as well as two- and three-component complexes on the wetting energy of the surfaces of aluminum oxide  $\text{Al}_2\text{O}_3$ , marble  $\text{CaCO}_3$  and quartz  $\text{SiO}_2$ .

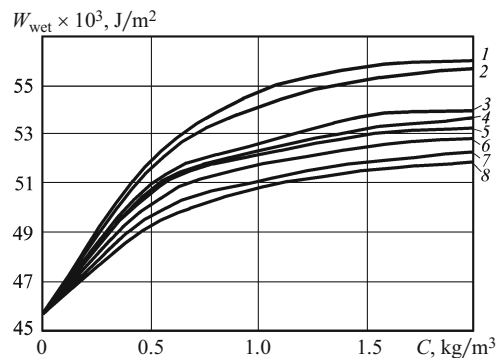
To determine indirectly the effect of the individual dispersers and organo-mineral complexes on the wetting energy of the surfaces we used a standard procedure to determine experimentally the dependence of the action of defloculators on the surface tension  $\sigma_{\text{liq-g}}$  at a liquid-gas interface and the contact angle  $\theta$  [8]. According to the equation we calculated the wetting energy

$$W_{\text{wet}} = \sigma_{\text{sol-g}} - \sigma_{\text{sol-liq}} = \sigma_{\text{liq-g}} \cos \theta,$$

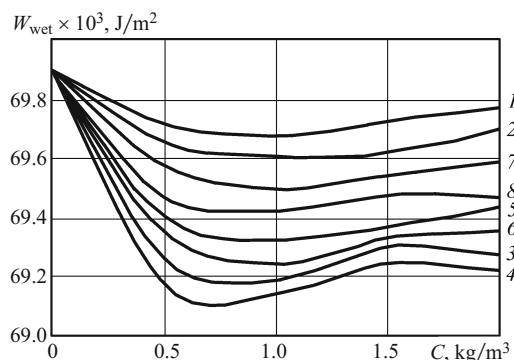
where the main parameters are the values of the specific free surface energies on solid phase – gas interface  $\sigma_{\text{sol-g}}$ , liquid-gas interface  $\sigma_{\text{liq-g}}$  and solid – liquid interface  $\sigma_{\text{sol-liq}}$ .

The results of the investigations of the effect of the individual components of the complexes SB-FF, SB-5, STPP and NaOH and complex organo-mineral defloculators SB-FF + STPP, SB-5 + STPP, SB-FF + STPP + NaOH and SB-5 + STPP + NaOH on the wetting energy of the surfaces of aluminum oxide, marble and quartz are presented in Figs. 1 – 3.

These investigations showed (see Fig. 1) that solutions of two-component complexes SB-FF + STPP and SB-5 + STPP and three-component complexes SB-FF + STPP + NaOH and SB-5 + STPP + NaOH of defloculators increase the wetting energy of the surface of aluminum oxide more than the total increase of the wetting energy of the experimental surface by solutions containing SB-FF, SB-5, STPP and NaOH separately. As a result, the phenomenon of synergism is observed in the effect of complex organo-mineral defloculators on the wetting energy of the  $\text{Al}_2\text{O}_3$  surface. In addition, the value of the wetting energy of three-component organo-mineral de-



**Fig. 2.** Effect of the content  $C$  of different additives on the wetting energy  $W_{\text{wet}}$  of the surface of marble  $\text{CaCO}_3$ : 1) SB-FF; 2) SB-5; 3) STPP; 4) NaOH; 5) SB-FF + STPP; 6) SB-5 + STPP; 7) SB-FF + STPP + NaOH; 8) SB-5 + STPP + NaOH.



**Fig. 3.** Effect of the content  $C$  of different additives on the wetting energy  $W_{\text{wet}}$  of the surface of  $\text{SiO}_2$ : 1) SB-FF; 2) SB-5; 3) STPP; 4) NaOH; 5) SB-FF + STPP; 6) SB-5 + STPP; 7) SB-FF + STPP + NaOH; 8) SB-5 + STPP + NaOH.

floculators is greater than that of two-component complexes. This shows that synergism is strongest with the introduction of SB-FF + STPP + NaOH and SB-5 + STPP + NaOH in ceramic slips containing aluminum oxygen compounds. The increase in the wetting energy can also be an indirect confirmation of a reduction in the strength of individual contacts in the coagulation structures of polymineral suspensions accompanying the introduction of complex organo-mineral defloculators.

It is evident from Fig. 2 that the energy of wetting of a  $\text{CaCO}_3$  surface by solutions containing the complex organo-mineral defloculators does not increase compared with the total energy of wetting by solutions containing individual dispersers separately (SB-FF, SB-5, STPP and NaOH). In the course of these studies it was also found that the energy of wetting by the solutions SB-FF, SB-5, STPP and NaOH is higher than for solutions of complex organo-mineral defloculators.

The wetting energy of a quartz surface (see Fig. 3) remained practically unchanged when using solutions of complex organo-mineral defloculators and solutions of the indi-

vidual dispersers used separately in the experiments. For this reason the phenomenon of synergism is not observed for the combined action of the components of the complexes on the wetting energy of quartz. This is explained by the fact that a quartz surface is more hydrophyllic (contact angle  $\theta \approx 15^\circ$ ) than a marble surface ( $\theta \approx 48^\circ$ ) and an aluminum oxide surface ( $\theta \approx 54^\circ$ ). The complex organo-mineral deflocculators added to a solution do not cause further hydrophyllization of quartz, which already has a comparatively high surface hydrophobicity and the contact angle decreases very little because of the low surface activity of the complexes at the solution – air boundary.

In summary, the wetting energy of complex organo-mineral deflocculators on different surfaces has been determined experimentally. An increase of the wetting energy was found only on an  $\text{Al}_2\text{O}_3$  surface with the introduction of the complexes based on oxyphenolfurfural oligomers. This is proof of the phenomenon of synergism of complex organo-mineral deflocculators in polymineral systems containing aluminum oxygen compounds. In addition, the phenomenon of synergism is stronger in the three-component complex organo-mineral deflocculators than in two-component additions, which confirms that three-component complexes are more effective in ceramic slips.

It was proved that the two-component complexes SB-FF + STPP and SB-5 + STPP and the three-components deflocculators SB-FF + STPP + NaOH and SB-5 + STPP + NaOH operate in the ratios 1 : 4 and 1.3 : 3.75 : 1.5, respectively, in polymineral systems, where unsaturated active surface centers are associated with  $\text{Al}_2\text{O}_3$ . It is for such ratios that the complex organo-mineral deflocculators have the

greatest effect on the electrostatic and adsorption-solvate factors of aggregative stability, as a result of which the fluidity of ceramic slips containing aluminum oxygen compounds increases significantly.

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